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A coordination network containing metal–organometallic secondary building units based on π-bonded benzoquinone complexes

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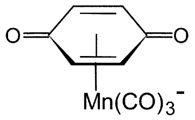
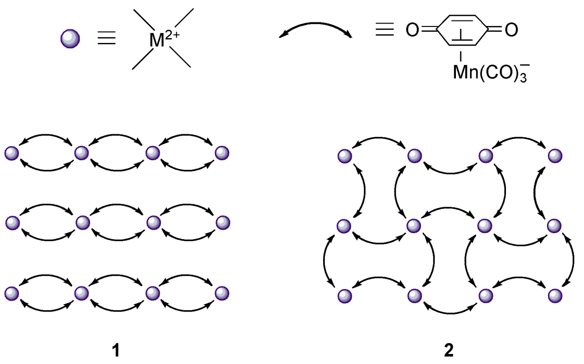
In DMSO–MeOH solvent the complex [(η^4-benzoquinone)Mn(CO)$_3$]$^-$ (QMTC) reacts with Mn^{2+} ions to produce the coordination polymer {Mn$_2$[(η^4-benzoquinone)Mn(CO)$_3$]$_4$(DMSO)}$_n$, which consists of dimanganese secondary building units interconnected by QMTC spacers.

Metal-directed self-assembly of finite and infinite networks has been used to generate materials that have many potential applications in magnetics, optics, catalysis, separations, and general guest–host interactions.[1–7] Many metal–organic networks based on metals or metal clusters connected by multifunctional organic ligands have been reported.[1–11] We recently demonstrated that the π-bonded organometallic complex (η^4-benzoquinone)Mn(CO)$_3^-$ (QMTC) can serve as a bifunctional ligand (organometalloligand) by coordinating through the quinoid oxygen atoms to metal ions to generate ‘metal–organometallic networks’ (MOMNs).[12,13] It was shown that in DMSO solvent QMTC can link together metal ions to give neutral 1D or 2D isomeric networks, **1** and **2** in Scheme 1. The metal ions in **1** and **2** can complete their coordination requirements *via* axial solvent ligands. Herein we report that under different experimental conditions QMTC combines with Mn^{2+} to afford a new polymeric structure containing an organometallic cluster that functions as a secondary building unit (SBU) in the construction of the novel diamondoid MOMN {Mn$_2$[(η^4-benzoquinone)Mn(CO)$_3$]$_4$(DMSO)}$_n$ (**3**).



QMTC

The new three-dimensional MOMN **3** was obtained by simple thermal treatment of neutral complex (η^5-semiquinone)Mn(CO)$_3$[14] at 75 °C in 1 : 1 DMSO–CH$_3$OH co-solvent under room light and air,† during which there was a slow photogeneration of Mn^{2+} ions, as shown by previous results.[12,13] MOMN **3** was also readily prepared from (η^5-semiquinone)Mn(CO)$_3$ in the presence of a half equivalent of Mn(OAc)$_2$·4H$_2$O under the same conditions. Fig. 1 shows a portion of the unit cell of **3**, which contains QMTC organometalloligands that serve as pairwise spacers to connect dimeric units of Mn^{2+} ions.‡ Fig. 2(a) illustrates the organometalloligand pairwise spacers in more detail. The novel feature of the structure is the presence of dimanganese units that are held in place by two quinone molecules that bridge the manganese atoms by coordination from the same oxygen (Fig. 2(b)). There



Scheme 1 A cartoon of coordination networks formed from M^{2+} ions and QMTC spacers.

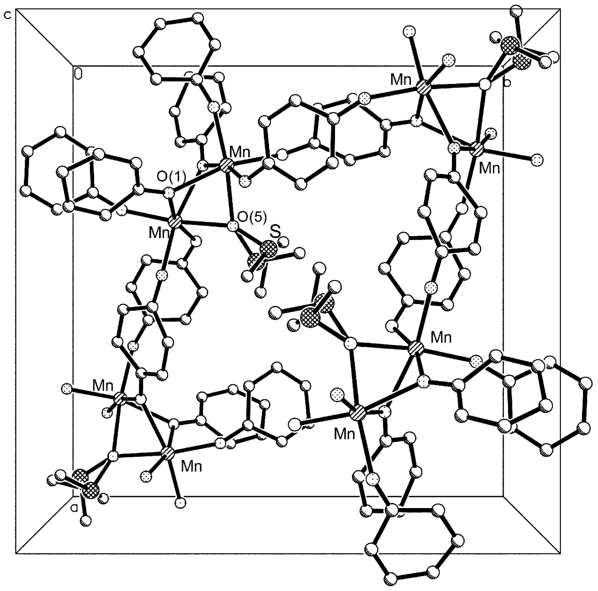


Fig. 1 Part of the unit cell contents of MOMN coordination polymer **3**, viewed down the *c* axis. Hydrogen atoms and Mn(CO)$_3$ groups are omitted in order to facilitate viewing the principal features of the 3D network. The DMSO ligand is disordered, as shown.

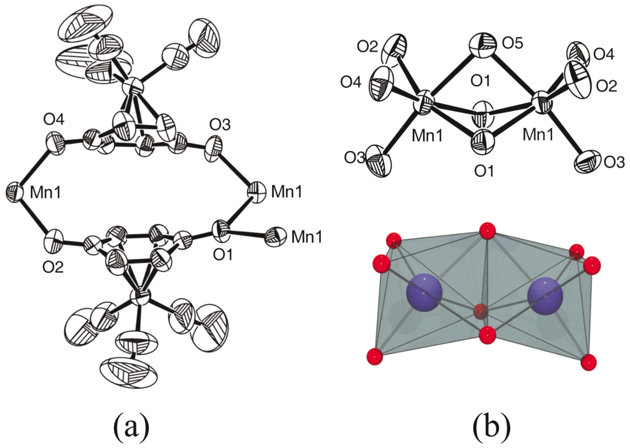


Fig. 2 The structure of **3** showing (a) the pairwise spacers that connect the dimanganese units and (b) a view of the coordination environment within the dimanganese units. Note that one QMTC ligand connects two Mn atoms while the other QMTC connects to three Mn atoms.

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is also a disordered bridging DMSO ligand. The resultant assembly constitutes an organometallic cluster that functions as a SBU that connects to other SBUs *via* the QMTC pairwise spacers. Heretofore, most metal–organic SBUs which build infinite networks have been based on carboxylate-bridged metal clusters.[8–11]

As shown in Fig. 2(b), the dimanganese cluster, which constitutes the core of the SBU, consists of two slightly distorted octahedra of oxygen atoms around each Mn center with one triangular face shared. Two types of QMTC spacers exist in **3**, one connecting to two Mn sites and another that connects to three Mn sites (Fig. 2(a)). In both types of QMTC organometalloligand the benzoquinone units adopt a boat conformation with the quinone carbons bent out of the diene plane by about 13° for the monodentate oxygens and by 16° for the bidentate oxygens, so that the overall structure is best described as η^4-quinone in both QMTC types. As would be expected, the Mn–O distances to the bridging quininoid oxygens (average 2.22 Å) are longer than those to the non-bridged oxygens (average 2.11 Å).

As stated above, the metal centers in each dimanganese unit are bridged by three oxygen atoms from two QMTC molecules and one DMSO molecule, with a Mn–Mn distance of 3.22 Å. The remaining six coordination sites in each dimanganese cluster are completed by QMTC bonding in a monodentate fashion. The basic SBU assembly possesses fourfold connectivity to adjacent SBUs, as illustrated in Fig. 3. Each dimanganese unit is separated by 9.60 Å from adjacent ones by four sets of QMTC pairwise spacers, which defines a pseudo-tetrahedral geometry.[15] This pattern produces spiral arrangements around fourfold screw axes, which link together to form the 3D diamondoid network shown in Fig. 4.

In conclusion, we have demonstrated the use of the organometalloligand QMTC to generate a 3D coordination network which contains a dimanganese cluster that functions as an *organometallic* secondary building unit.

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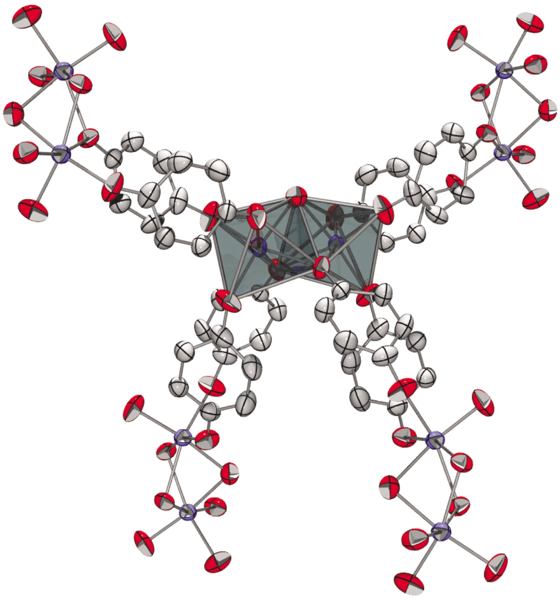

Fig. 3 Illustration of the pseudo-tetrahedral disposition of pairs of QMTC spacers from a dimanganese SBU in MOMN **3**. All hydrogen atoms and $Mn(CO)_3$ groups are omitted for clarity. Only the oxygen atom of the disordered bridging DMSO is shown. (Mn, blue; O, red; C, gray).

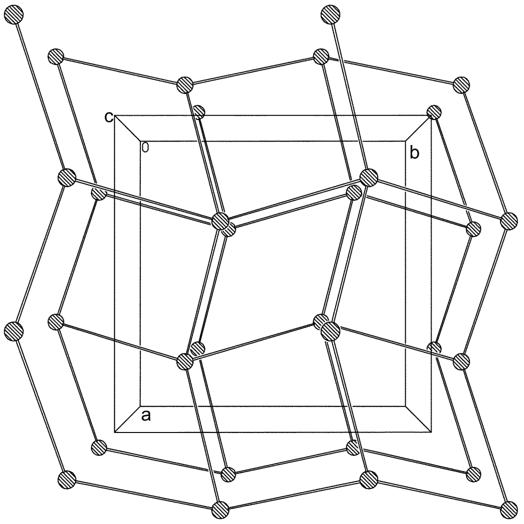

Fig. 4 Schematic representation of the 3D diamondoid network structure in **3**. Each pair of manganese atoms is represented by a ball at the midpoint, and is connected to neighboring pairs by a tetrahedral arrangement of pairwise QMTC linkages. The view is down the *c* axis, and parts of two layers normal to the axis are shown.

Notes and references

† The neutral complex (η^5-semiquinone)$Mn(CO)_3$[14] (15 mg, 0.060 mmol) was heated in DMSO–CH_3OH (0.3 mL: 0.3 mL) at 75 °C in room light. After 3 days, crystals of polymer **3** suitable for X-ray studies were obtained in 72% yield. IR (KBr) ν_{CO} 2030 (s), 1941 (s), 1560 (s), 1530 (m), 1517 (s), 1505 (s) cm^{-1}. Elemental analysis calc. (%) for **3**, $C_{19}H_{11}Mn_3O_{10.5}S_{0.5}$: C 38.80, H 1.89, S 2.73; found: C 38.40, H 2.05, S 3.09.

‡ Crystal data for **3**: formula $C_{19}H_{11}Mn_3O_{10.5}S_{0.5}$, M = 588.13, tetragonal, space group $P4_12_12$, a = 16.7980(3), b = 16.7980(3), c = 16.2379(6) Å, V = 4581.9(2) Å^3, Z = 8, ρ_{calc} = 1.705 g cm^{-3}, μ = 1.727 mm^{-1}, $F(000)$ = 2336, θ range 2.12–25.03°, 312 variables refined with 4056 independent reflections to final R indices $[I > 2\sigma(I)]$ of R_1 = 0.0469 and wR_2 = 0.1179, and GOF = 1.048. Crystals of **3** suitable for X-ray studies were grown from DMSO–CH_3OH solutions. X-Ray data collection with Mo K_α radiation was carried out at 298 K using a Bruker Apex diffractometer equipped with a CCD area detector. Structures were determined by direct methods and refined on F^2. CCDC 189526. See http://www.rsc.org/suppdata/cc/b2/b206458h/ for crystallographic data in CIF or other electronic format.

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